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Applicability of polydimethylsiloxane (PDMS) and polyethersulfone (PES) as passive samplers of more hydrophobic organic compounds in intertidal estuarine environments

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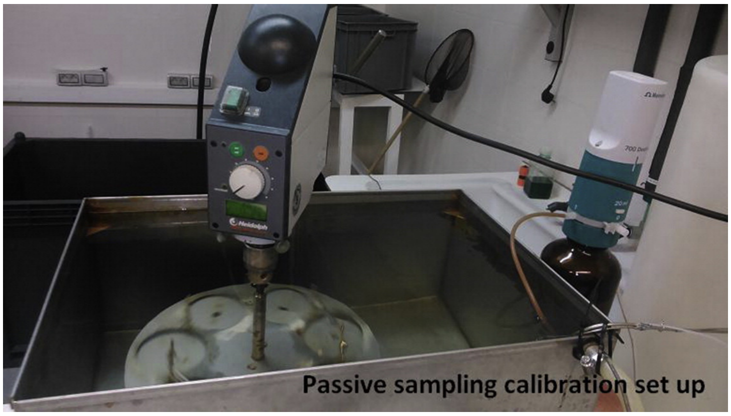
HIGHLIGHTS

- Sampling rates of contaminants were calculated in different aquatic systems.
- The suitability of deuterated PAHs as PRC compounds in seawater was studied.
- The effect of the salinity in sampling rates was analyzed.
- TWA concentrations and grab sampling concentrations were compared in seawater.

GRAPHICAL ABSTRACT



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ABSTRACT

The uptake calibration of three passive samplers, stir-bars, MESCO/stir-bars and polyethersulfone tubes (PES_t), was assessed in seawater at different salinities for 17 organic compounds including organochlorine compounds, pesticides, phthalates, musk fragrances and triclosan. The calibration procedure was accomplished by exposing the samplers to a continuous flow of fortified seawater for up to 14 days under laboratory conditions. Prior to the exposure, stir-bars and MESCO/stir-bars were loaded with a known amount of deuterated PAH mixture as performance reference compounds (PRC). For most of the studied compounds, the sampling rates (Rs, $\mathrm{mL \cdot day^{-1}}$) were determined for each sampler at two salinities (15 and 30‰) and two nominal concentrations (25 and 50 $\mathrm{ng \cdot L^{-1}}$). Among the tested devices, though PES can be an outstanding cheap alternative to other passive samplers, naked or free stir-bars provided the best results in terms of uptake rates (i.e., the Rs values ranged from 30 to 350 $\mathrm{mL \cdot day^{-1}}$). Regarding the variation of the salinity, the Rs values obtained with naked stir-bars were statistically comparable in the full range of salinities (0–30‰) but the values obtained with MESCO/stir-bars and PES_t were salinity dependent. Consequently, only stir-bars assured the required robustness to be used as passive samplers in intertidal estuarine environments. Finally, the stir-bars were applied to estimate the

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Polyethersulfone
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time-weighted average concentration of some of those contaminants in the feeding seawater of the experimental aquaria at the Plentzia Marine Station (Basque Country) and low levels of musks fragrances (0.1–0.2 ng·L^{-1}) were estimated.

1. Introduction

Passive sampling has become a promising approach to estimate time-weighted average concentrations (C_{TWA}) in water streams and porewater (Jacquet et al., 2014; Oen et al., 2011). However, there are still many pitfalls to overcome and many opportunities to gain, especially when the shortcomings of direct sampling approaches are considered (Mills et al., 2014).

One of the pitfalls is directly related with the measurement problem as pointed by Harman et al. (2012a). This problem can be easily explained when very low concentrations are being measured or when the spatial and/or temporal variations are much larger than the sampling precision. Additionally, we can also challenge the real meaning of the fraction that is really measured and its relevance, in particular the ranges of fractions going from the free-available concentration to the total concentration, and the links of these values with the accumulation in aquatic organisms (Claessens et al., 2015; Jin et al., 2015).

Another important issue is the split behavior of polar and non-polar contaminants and the sorptive phases required to achieve an efficient sampling. In this sense, the sampling of non-polar contaminants gains the favor of the easier modeling of partition equilibria, as recently described by Booij and Smedes (2010), and the use of triolein filled semipermeable membrane devices (SPMD), low density polyethylene (LDPE) and polydimethylsiloxane (PDMS) or silicone based materials (sheets, rods, magnetic bars, etc.), either naked or wrapped in LDPE and known as MESCO (Membrane Enclosed Sorptive Coating), is widely accepted (Allan et al., 2009; Paschke et al., 2007; Posada-Ureta et al., 2016). On the contrary, the sorption of polar contaminants is ruled by different interactions (hydrogen bonding, ion pairing, electrostatic forces, van der Waals interactions…) and the uptake process is dominated by adsorption at the surface of collecting phase. Consequently, different sorptive samplers as polar organic integrative samplers (POCIS) or polyethersulfone (PES) membrane are used (Harman et al., 2012b; Morrison and Belden, 2016).

In spite of the many difficulties that we are aware of when passive sampling is being used, it is still a promising approach because: (i) it is an affordable way to estimate average concentrations of a wide range of analytes, (ii) their design allows long exposure periods without hardly any intervention, and (iii) it enables the detection of trace organic contaminants that otherwise would have been missed due to the detection limits in the conventional analysis of grab samples. Consequently, there are many recent contributions describing the use of passive samplers in different aquatic media (Allan et al., 2013; Bruemmer et al., 2015; Estoppey et al., 2015; Moschet et al., 2015) since the calibration can be suited to coastal or continental aquatic media and it may include the QA/QC procedures to assure the fit-for-purpose (Roll and Halden, 2016; Vrana et al., 2016). In this sense, reliable performance reference compounds (PRCs) are often included to compensate the hydrodynamic variations on the sampling rates (Rs) that may happen from the laboratory calibration to the field application (Vrana et al., 2006). All the details regarding the theoretical modeling of the uptake and release processes in passive sampling are available in the Supplementary material S1.

However, the application of passive sampling in estuaries shows the problem of the periodic variation of the salinity and the temperature. Though the "salting-out" effect has been considered negligible in terms of the variation of the partition coefficients in solid-phase microextraction (SPME) studies (DiFilippo and Eganhouse, 2010; Lohmann et al., 2012), the effect of the variation of temperature and, specifically, the slight effect of salinity has been recently pointed with silicone rubber samplers (Jonker et al., 2015) based on partition coefficients. Moreover, uptake calibration experiments in salt water were recently performed in order to assure the suitability of Chemcatcher® to monitor hydrophobic pollutants in fresh and salt water (Petersen et al., 2015). However, we believe that the variation of salinity in estuaries requires a deeper attention and it is worth studying this effect, especially when high and periodic gradients of salinities may affect the uptake and release kinetics of the contaminants. The scope of this work, therefore, is based on the kinetic pattern i.e. following a thorough estimation of the Rs values and the elimination rate constants (k_e) of the PRCs at different salinities instead of studying the variation of the partition coefficients.

Consequently, following the passive sampling set up previously used to study the performance of different passive samplers for hydrophobic compounds (Posada-Ureta et al., 2016), we wanted to study the effect of the salinity to support the suitability of PDMS (stir-bars), both free or naked stir-bars and MESCO/stir-bars, and PES polymers to monitor a broad variety of hydrophobic organic contaminants often found in estuarine and coastal media. The list of contaminants includes organochlorine pesticides (DDT related), organophosphorous pesticides, hexachlorohexanes (HCH related), phthalates, antimicrobials, alkylphenols, musk fragrances and triclosan.

2. Experimental work

2.1. Reagents and materials

All the laboratory material was washed with abundant Ellix quality water (<0.2 μS cm^{-1}, Millipore, Bedford, MA, USA) and then sonicated under clean acetone (Q.P., Panreac Química, Barcelona, Spain) for at least an hour or maintained in a clean acetone bath overnight. After that, the material was rinsed with ultra-pure water (<0.057 μS cm^{-1}, Milli-Q Model 185, Millipore, Bedford, MA, USA). Finally, the glass material was dried in an oven at 400 °C for at least 4 h and stored. In addition, the use of perfumes by laboratory personnel was restricted.

Regarding the chemical standards used, 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphtalene (AHTN, tonalide®, 97.9%) and 1,3,4,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(γ)-2-benzopyran (HHCB, galaxolide®, 53.5%) were obtained from LGC Standards GmbH (Wesel, Germany). The four organochlorine pesticides: o,p′-dichlorodiphenyldichloroethane (2,4′-DDD, 99%), p,p′-dichlorodiphenyldichloroethane (4,4′-DDD, 99%), p,p′-dichlorodiphenyldichloroethylene (4,4′-DDE, 99.7%) and p,p′-dichlorodiphenyltrichloroethane (4,4′-DDT, 99%) were supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany). The four hexachlorocyclohexane compounds: α-hexachlorocyclohexane (α-HCH, 99.5%), β-hexachlorocyclohexane (β-HCH, 99.5%), γ-hexachlorocyclohexane (γ-HCH, 99.5%) and δ-hexachlorocyclohexane (δ-HCH, 99.5%) were obtained from Fluka (Steinheim, Germany). The two phthalates: benzyl-2-butyl phthalate (BBP, 98%) and di-octyl phthalate (DOP, 98%) and the two alkylphenols: 4-tert-octylphenol (4tOP, 97%) and 4-n-octylphenol (4nOP, 99%) were purchased from Alfa-Aesar (Karlsruhe, Germany). The antimicrobial triclosan (triclos, 97%) was obtained from Sigma Aldrich (Steinheim, Germany). The two organophosphorous pesticides: Chlorpyrifos (Chlorp, 99%, Pestanal®) and Chlorfenvinphos (Chlorf, 97.3%) were provided by Sigma-Aldrich (Seelze, Germany). Isotopically

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